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Mesoscopic theory of percolation currents associated with quantitative description of VAGs: Confirmation on real data

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ABSTRACT

The general mesoscopic theory pretending on the *quantitative* description of the interfacial surface and the self-similar structure of the double electric layer in the vicinity of solid electrodes is suggested. It takes into account the fact that the fractal dimension can be complex and depends on the applied potential. In the frame of the suggested theory, the fitting function pretending on description of the VAGs was found. It was applied for the fitting of original experimental data related to detection of the Cd^{+} ions in different concentrations in the KCl solution. The assumptions and possible applications of the suggested theory to description of other measured data are discussed.

1. Introduction and formulation of the problem

The development of the mathematical methods associated with quantitative description of the measured VAGs was aimed presumably for increasing of their sensitivity and resolution when one material of electrodes was replaced by another one. Another important target was related also with variations of the temporal conditions during of the registration process that can change also the form of the registered VAGs. In the result of the long standing, research the basic analytical equations were obtained in the explicit or numerical form [1]. They connect the value of the peak current with the parameters of the investigated solution, geometry of measured device and the type of electrochemical cell. The form and the shape of the measured VAG depends essentially on the size (macro(10^{-2} m)-micro(10^{-6} m)-ultra-micro(10^{-8} m)) and geometry (plane, disc-shaped, cylindrical spherical and their modifications as stripe-shaped) of the used electrodes [2]. We should mark here that this conventional system of electrodes classification solves partially the questions related to their sensitivity if the conditions of the registration of the corresponding VAGs follow to their reproducibility and the absence of the potential overlapping. The two last features improve the signal/noise ratio. In the case of the overlapping signals, the effective mathematical methods and the corresponding software extracting the peaks of the desired micro-components were developed [3]. However, these methods of the mathematical modeling have presumably *phenomenological* character and are "tuned" for extraction of physical/chemical parameters if the concentration of the detected reagents are rather high.

In any case, the results of any voltammetric experiment will depend essentially on the structure of the interfacial area defined as the double-electric layer (DEL). In the modern literature, there are many specific models related to definition and formation of the specific DEL near the electrodes [4–6] but up to now, a "universal" model of the DEL that can be used in many experimental situations is *absent*. But based on the results of different experimental methods, it was proved that the structure of the DEL depends essentially on the material used for preparation of solid electrodes, its porosity/surface irregularity, the presence of the absorbed organic/nonorganic films on its surface, the nature of the background electrolyte and the covering solution and, therefore, the interest for understanding of the DEL nature is *not* depleted. For deeper understanding the problem posed in this paper, it is appropriate to cite the important remark of the Z. Stojek given in the well-known book [7]: "*there is still much able to predict the behavior and the capacitance of the double layer in the entire available po-*

The basic acronyms: BLC, bell-like curve; DEL, double electric layer; FLSM, the functional least square method; GCE, glassy carbon electrode; LLSM, the linear least square method; IM, intermediate model; VAGs, voltammogram(s).

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